The University of Chicago

STUDIES IN THE SYSTEM, CALCIUM, CALCIUM HYDRIDE, HYDROGEN

A DISSERTATION SUBMITTED TO THE FACULTY
OF THE DIVISION OF THE PHYSICAL SCIENCES
IN CANDIDACY FOR THE DEGREE OF DOCTOR
OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY
1931

By
MORRIS FRANK STUBBS

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INTRODUCTION

A survey of the literature shows that there is a wide variation in the results which have been obtained by the different investigators who have studied the reaction between calcium and hydrogen, as well as in the results which have been obtained for the dissociation pressures of the resulting hydride.

The differences found may be classed under two heads (1) the temperature at which calcium combines with hydrogen, including the rate of reaction at different temperatures and (2) the dissociation pressures of calcium hydride obtained. The studies of the dissociation pressures also involve the effect of varying amounts of free calcium in the system, as well as the possibility of the existence of a lower hydride.

B. von Lengyel[1] states that metallic calcium absorbs hydrogen slowly at ordinary temperatures and rapidly at a dull red heat. Sieverts[2] found that calcium absorbs hydrogen at room temperature and takes it on at much greater speed from 150°-300° C. Ephriam and Michel[3] state that the action up

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1. B. von Lengyel, Math. Ber. Ungarn., 14, 180 (1898)
2. Sieverts, Z. Electrochem., 22, 15 (1916)
3. Ephriam and Michel, Helv. Chim. Acta, 4, 907 (1921)

to 300° is very likely an adsorption, rather than a chemical union. The speed of reaction was found to decrease up to 600° C. above which temperature it became more rapid. Hüttig and Brodkorb[1] state that no hydrogen absorption was found below 380° C., but that a brisk absorption occurred between 380°-450° C. Brönsted[2] states that hydride formation begins at about 400° C. when calcium metal in compact form is heated in a stream of hydrogen. Kassner and Stempel[3] showed that calcium filings react rapidly and quantitatively at 270° C to form calcium hydride. The speed of reaction was found to decrease with increasing temperature up to the region of the melting point of calcium (805° C.), where the speed of absorption is very great.

Equilibrium measurements on the system calcium hydride, calcium, hydrogen were first carried out by Moldenhauer and Roll-Hansen.[4] These investigators obtained pressure measurements which seemed to be quite reproducable. Pressure measurements with a substance containing only one half as much hydrogen as required for normal calcium hydride (CaH_2) gave values which were of the order of magnitude of one half of those obtained with the normal hydride.

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1. Hüttig and Brodkorb, Z. anorg. allgem. Chem., 153,309(1926)
2. Brönsted, Z. Electrochem., 20, 81 (1914)
3. Kassner and Stempel, Z. anorg. allgem. Chem.,181,83(1929)
4. Moldenhauer and Roll-Hansen, Z. anorg. Chem.,, 82,130(1913)

These results led Moldenhauer and Roll-Hansen to conclude that a sub-hydride, CaH, existed and that the two series of pressure measurements obtained correspond to the following equilibria: (1) $CaH_2 \rightleftharpoons CaH + \frac{1}{2}H_2$. (2) $CaH \rightleftharpoons Ca + \frac{1}{2}H_2$. These workers used a porcelain reaction tube lined with a thin shell of iron to prevent the calcium hydride from reacting with the porcelain.

Brönsted[1] obtained dissociation pressure measurements in the region from 641°-747° C. The equilibrium values were reached quickly by raising and lowering the temperature. The results in general agree with the first series obtained by Moldenhauer and Roll-Hansen, but do not support the conclusion that calcium sub-hydride is formed.

Ephriam and Michel[2] virtually repeated the work of Moldenhauer and Roll-Hansen and found that partial removal of hydrogen from the normal hydride caused a large decrease in the dissociation pressures. These investigators concluded that the hydride and metal appear to form a complete series of solid solutions, with the value of the dissociation pressure dependent on the amount of excess calcium. No evidence of the existence of a lower hydride was found.

Kraus and Hurd[3] measured the dissociation pressures of

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1. Brönsted, loc. cit.
2. Ephriam and Michel, loc. cit.
3. Kraus and Hurd, J. Am. Chem. Soc., 45, 2559 (1923)

an approximately 90 percent calcium hydride mixed with about one third of its weight of fresh calcium filings. Evidence was obtained of definite reproducable equilibrium pressures involving hydrogen and calcium hydride. These workers state that the third phase is uncertain, but that the conditions of the experiment render it probable that a sub-hydride of calcium exists. An iron cylinder, open at one end, was used as a container for the calcium hydride. This precaution was taken to prevent the calcium hydride from reacting with the quartz reaction tube.

Hüttig and Brodkorb[1] claim that calcium hydride has a measureable pressure, even at room temperature. At 20° C. the hydrogen pressure was found to rise continuously for nine days without reaching a constant value. These writers are of the opinion that calcium hydride is an ideal limiting compound, the actual compound showing a smaller hydrogen content. It is claimed that when a small amount of hydrogen is pumped off from calcium hydride that a single hydrogen-poor phase is first formed. This single phase then separates slowly into two phases, one rich and one poor in hydrogen. The rich phase is supposed to be nearly pure calcium hydride and the poor phase another compound which holds hydrogen much tighter than calcium hydride.

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1. Hüttig and Brodkorb, loc. cit.

Kassner and Stempel,[1] using a partially hydrogenated calcium, obtained dissociation pressures of the same order of magnitude as those obtained by the previous workers. When a 97 percent hydride was used a reproducable equilibrium curve with much higher pressures was obtained. No transition to the lower curve was found on pumping off hydrogen. These authors believe that the higher curve represents the true equilibrium: $2CaH_2 \rightleftharpoons 2CaH + H_2$ and that the lower values obtained by the other investigators are representative of the second dissociation: $2CaH \rightleftharpoons 2Ca + H_2$.

Quite recently Remy-Cennette,[2] as well as Hurd and Walker,[3] have taken special precaution to avoid possible errors which might be due to the sublimation of the solid products on to the walls of the quartz reaction tube. Remy-Cennette hydrogenated calcium in a closed iron tube, permeable to hydrogen, but not to calcium or calcium hydride. Hurd and Walker used a closed nickel cylinder. These investigators found somewhat higher values than those obtained by Kraus and Hurd, but much lower than those of Kassner and Stempel, who used samples of calcium hydride of high hydrogen content. Both Remy-Cennette and Hurd and Walker found the dissociation

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1. Kassner and Stempel, loc. cit.
2. Remy-Cennette, Compt. rend., 189, 579 (1929)
3. Hurd and Walker, J. Am. Chem. Soc., 53, 1685 (1931)

pressure to be practically independent of the quantity of metal present. Hurd and Walker state that the pressure re-established itself slowly with only 20 percent of the hydrogen present necessary to form normal calcium hydride. The results obtained by these workers show the presence of only one equilibrium curve.

As stated previously, it may be seen that the results recorded by several investigators differ widely. The results are at variance in regard to: (1) the temperature at which hydride formation begins; (2) the effect of free calcium on the equilibrium values and; (3) the possibility of two equilibrium curves, the second of which is thought to involve a lower hydride. The present study was undertaken as an attempt to clarify the divergent results found in the literature. The following studies were made in order to accomplish this purpose:

(1) The preparation of calcium of high purity.

(2) The adsorption of hydrogen by calcium at different temperatures.

(3) The determination of apparent equilibrium pressures of a 85 percent hydride-15 percent calcium mixture at different temperatures.

(4) Attempts to obtain equilibrium pressures for a calcium hydride of high hydrogen content.

(5) Attempts to prepare a sub-hydride of calcium.

(a) By adding approximately one half the theoretical amount of hydrogen necessary to form the normal hydride, at a pressure less than the apparent equilibrium pressure of the normal hydride.

(b) By removal of hydrogen from normal calcium hydride.

APPARATUS AND MATERIALS

Apparatus for Distillation of Calcium.- It was thought best to prepare a special pure calcium for use in some of the experiments. Pure calcium was obtained by vacuum distillation of a 97 percent calcium obtained from the American Magnesium Corporation. The still used consisted of a hollow cylinder of carbon free Swedish iron 12 inches long, of $1\frac{1}{2}$ inches outside diameter and $1\frac{1}{4}$ inches inside diameter as shown in figure 1.

A charge of approximately 10 grams of calcium was placed in the cylinder A, the condenser B was then screwed down tight and sealed with Picein cement. This done the still was placed in an upright electric furnace and connected to the vacuum line. When the pressure reached 10^{-3} mm. Hg, a rapid stream of water was started through the condenser and the furnace gradually heated to 750°-800° C. This temperature was maintained for approximately one hour, with the vacuum pumps in operation, during which time the calcium sublimed

Fig. 1.- Apparatus for distillation of calcium

on to the bottom of the condenser. The furnace was then cooled to room temperature and the still filled with butane gas. It was found that the distilled calcium was so active that a part of it was converted into oxide and nitride, in spite of the fact that the still was opened and the calcium removed as quickly as possible after disconnecting from the vacuum line. The atmosphere of heavy butane kept the calcium in a pure condition. Radial crystals of pure white metal with a thin layer of dark brown outer crust were obtained. The crust was cut off and only the pure white metal used.

Analysis.- Several undistilled and distilled samples of calcium were analyzed by the usual gravimetric method. The sample was put into solution, precipitated as oxalate and ignited to oxide with the following results:

Undistilled Calcium

Anal. Subs., 0.6423, 0.5402, 0.5965. Calcd. for Ca, 100.00. Found: 97.15, 97.30, 97.19.

Distilled Calcium

Anal. Subs., 0.2752, 0.2666, 0.9132, 0.6555. Calcd. for Ca, 100.00. Found: 99.38, 99.16, 99.47, 99.54.

Qualitative tests showed the presence of small amounts of chloride, oxide and nitride in the undistilled samples. These impurities were found to have been removed by distillation of the metal.

Apparatus for Purification of Hydrogen.- Electrolytic

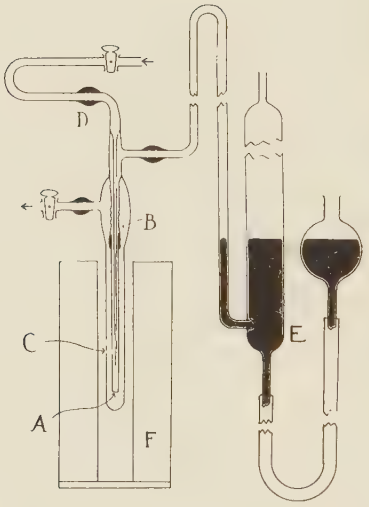

Fig. 2.- Apparatus for purification of hydrogen

hydrogen was purified by diffusion through a heated palladium tube as shown in figure 2. The apparatus, with several modifications, was patterned after that of Kraus and Lucasse.[1] The palladium tube A was fused to a lead glass which was connected, in turn, to a quartz tube by means of the graded seal B. The quartz chamber C was evacuated and hydrogen conducted in through the quartz capillary D to the bottom of the palladium tube. The excess hydrogen was allowed to bubble off through the blow-off tube E under an excess pressure of about 25 centimeters of mercury. The electric furnace F was then heated to a dull red. Under these conditions hydrogen diffused rapidly through the palladium tube into the quartz chamber C from which it was led into the line and reservoirs as indicated by the arrow. All quartz to pyrex seals were made with de Khotinsky cement. The apparatus described is easy to manipulate and gives a very pure product.

Apparatus for Preparation of Calcium Hydride and Determination of Dissociation Pressures.- The apparatus used for the preparation of calcium hydride and the determination of dissociation pressures is shown in figure 3. Weighed amounts of calcium were placed in the pure iron tube A, which was then quickly lowered into the clear quartz tube B, of 2.2

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1. Kraus and Lucasse, J. Am. Chem. Soc., 44, 1941 (1922)

centimeters inside diameter and 32 centimeters length. The quartz tube was then connected to the rest of the system by means of the ground glass joint C and immediately evacuated through D with a three stage mercury vapor pump, backed by a Cenco Hy-Vac pump. The stop-cock E was then closed and purified hydrogen admitted to the calibrated reservoirs F and G. The hydrogen pressure was measured on the vacuum type manometer H. This manometer was checked against a high vacuum at frequent intervals. The calibrated reservoir I was used for removing hydrogen from the reaction tube. The volume of the line and manometer were carefully calibrated, so that it was possible to admit or withdraw known volumes of hydrogen as desired.

The temperature, which was kept constant by means of a variable resistance, was measured with a platinum-platinum rhodium thermocouple, calibrated with Bureau of Standards metals. The hot junction of the thermocouple was placed next to the quartz tube A, opposite the iron reaction tube. The cold junction was kept in a Dewar tube containing ice and water. The E.M.F. developed was measured with a White potentiometer. The space between the quartz tube and the mouth of the furnace was packed with asbestos wool in order to minimize circulation. The temperature at different points within the furnace varied but a few degrees.

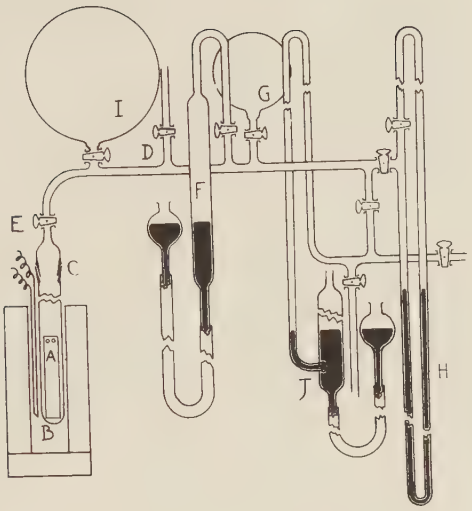

Fig. 3.- Apparatus for preparation of calcium hydride and determination of dissociation pressures

EXPERIMENTAL

Adsorption of Hydrogen by Calcium at Room Temperature.- In order to test the action of calcium toward hydrogen at room temperature, calcium filings were placed in the quartz reaction tube, which was then evacuated and filled with purified hydrogen. The filings were then allowed to remain in contact with the hydrogen for a considerable length of time. No hydrogen was adsorbed under these conditions as shown by the results in Table I. The apparatus was tested for leaks before and after each experiment.

Table I

Action of Hydrogen on Calcium Filings at Room Temperature

Weight of Ca used	H_2 Pressure (cm.Hg) original	final	Time hrs.	Temperature °C.
undistilled 0.1620g.	90.15	90.15	48	28°
distilled 1.4265g.	73.30	73.30	20	26°

It was next decided to put the calcium in a very finely divided condition. This was done by dissolving the metal in liquid ammonia and then allowing the ammonia to distill off gently at -33°C. through the blow-off tube J (figure 3), leaving the calcium in a very finely divided form on the walls of the quartz tube. The remainder of the ammonia was then removed by pumping at room temperature for several hours. The system was filled with hydrogen and

allowed to stand at room temperature for several days. Large volumes of hydrogen were adsorbed under these conditions as shown by the results given in Table II.

Table II

Adsorption of H_2 by Finely Divided Calcium at Room Temperature

Weight of Samples used	Volume H_2 adsorbed	Time hrs.	Percent Calculated for CaH_2
0.4573g.	54.3cc.	93	21.2
0.8242g.	278.7cc.	178	60.5
0.1846g.	55.0cc.	190	53.2

The apparatus was tested for leaks before and after each experiment. Calcium hydride did not form during the course of the experiments as evidenced by the fact that no white compound was produced, the calcium remaining dark gray in color. The phenomenon observed is evidently one of surface adsorption. After the finely divided calcium had stood for several days a few white specks were observed next to the wall of the quartz tube. Subsequent analysis showed these spots to be calcium amide, approximately 2 percent of the calcium being slowly converted into amide by the small amount of ammonia which was not removed, even after pumping for 23 hours in one case.

In order to determine if the calcium amide had adsorbed any of the hydrogen a sample of pure calcium amide was prepared by dissolving a 0.5467 gram sample of calcium in liquid ammonia in the presence of a rusty iron nail as catalyst. The resulting calcium amide was allowed to stand

in an atmosphere of ammonia for three days to insure complete conversion of all calcium to the amide. The ammonia was then pumped off for five hours and the resulting amide treated with hydrogen at a pressure of 82.7 centimeters of mercury. No adsorption of hydrogen took place in 240 hours.

It may be concluded that ordinary calcium filings will not adsorb hydrogen at room temperature, but that very finely divided calcium will adsorb varying amounts depending upon the state of subdivision of the metal and the length of time the calcium remains in contact with the hydrogen. In no case is there any evidence of hydride formation.

Action of Hydrogen Toward Calcium in the Region of 250°C.- Several experiments were carried out to determine the temperature at which hydride formation begins and to measure the speed of reaction in this temperature region. Weighed amounts of calcium were placed in the pure iron cylinder and lowered quickly into the quartz tube. The quartz tube was then attached to the vacuum line and evacuated. The furnace was heated to constant temperature and hydrogen admitted from a reservoir. The amount of hydrogen taken up was measured at definite time intervals by the decrease in pressure. It was found that the distilled calcium began to react at 200°-205° C., while the undistilled calcium filings first reacted at approximately 240°-250° C. Table III gives the temperatures used and the percent of calcium converted into calcium hydride at definite time intervals. The

results show that the speed of reaction is very great in the region from 250°-300°C. and especially so with the distilled samples. The heat of formation was sufficient to heat the mass to glowing in several cases. Quantitative conversion to hydride was probably not accomplished at these temperatures on account of the final low pressure of the hydrogen. Some of the first samples of distilled calcium were not protected in an atmosphere of butane gas while being removed from the still, so that some oxide and nitride were undoubtedly present.

Table III

Absorption of Hydrogen by Calcium in the Region of 250°C.

Undistilled Calcium

Weight of Ca used	Temp. °C.	Time in minutes 5	10	20	30	60	120	240
		Percent Calculated for CaH_2						
1.1500g.	250°	6.6	39.8	63.8	72.9	84.9	87.1	---
0.6379	270°	3.4	12.7	56.6	75.2	85.0	85.5	---
1.0178g.	270°	14.8	48.3	74.2	83.5	89.0	90.0	---
0.7662g.	270°	26.4	47.6	75.7	85.3	89.0	89.0	---
1.0364g.	360°	7.8	15.1	27.1	40.1	60.3	74.7	81.6

Distilled Calcium

Weight of Ca used	Temp. °C.	Time in minutes 2	5	10	20	30	60	120
		Percent Calculated for CaH_2						
1.4265g.	230°	----	---	23.1	----	63.8	----	95.3
1.1029g.	250°	66.6	69.9	----	----	74.9	76.6	78.0
1.7631g.	250°	61.1	----	----	----	----	----	93.0
0.6573g.	250°	----	37.0	66.6	81.6	82.6	82.6	82.6
0.7531g.	250°	76.2	----	----	----	----	----	93.0
1.3925g.	270°	----	79.7	81.3	----	83.4	84.0	84.0

In general the results obtained agree with those of Kassner and Stempel, although they are not comparable, since these workers carried out their experiments at constant pressure.

The Determination of Apparent Equilibrium Pressures of 85 Percent Hydride-15 Percent Calcium Mixtures at Different Temperatures.- An 85 percent calcium hydride, prepared as described previously, was heated slowly to 700°C while attached to the vacuum pumps, in order to remove adsorbed gases. Apparent equilibrium values were then obtained by heating the furnace to a definite temperature and reading the pressure after it had reached a constant value. One or two cubic centimeters of hydrogen were then removed by allowing the gas to expand into an evacuated reservoir. Pressure readings were again recorded when a constant value was reached. The reaction tube was then heated or cooled to a new temperature and the process repeated. The apparent equilibrium was found to establish itself quickly at the higher temperatures, while several hours were required at the lower temperatures.

Table IV gives the temperatures and corresponding apparent equilibrium pressures in centimeters of mercury obtained with three different samples of approximately 85 percent calcium hydride-15 percent calcium mixtures. The corresponding values obtained by Kraus and Hurd are listed for comparison. Series 1 was obtained by heating the furnace to 960°C. and then lowering the temperature to obtain the remaining values. Series 2 and 3 were obtained at the lower

temperatures first, the furnace then being heated to obtain the higher values. The experiments of Kraus and Hurd were carried out in the same manner as Series 1.

Table IV

Apparent Equilibrium Pressures at Different Temperatures

	Series 1	Series 2	Series 3	Kraus and Hurd
Temperature °C.	Pressure cm.Hg	Pressure cm.Hg	Pressure cm.Hg	Pressure cm.Hg
960°	34.65	27.40	-----	34.04
931°	23.05	19.25	-----	22.36
905°	15.20	13.35	11.70	14.08
871°	8.65	8.55	7.20	8.40
844°	5.40	5.75	-----	4.82
834°	-----	-----	3.60	3.76
792°	2.05	2.10	1.55	1.52
770°	1.30	-----	-----	0.93
734°	-----	-----	0.60	0.42

The lower pressures found at the higher temperatures in Series 2 and 3 are no doubt due to the fact that considerable hydrogen had been removed before reaching the higher temperatures. It was found that the pressure did not come back to its original value if large quantities of hydrogen were removed. This result indicates that the values obtained are not those of a true equilibrium.

Attempts to Obtain Equilibrium Pressures of a Calcium Hydride of High Hydrogen Content.- The samples of calcium hydride of high hydrogen content were obtained by heating distilled calcium at 250° C. with purified hydrogen under high pressure. The dissociation pressures obtained with 1.4265

grams of a 95.3 percent hydride are given in Table V.

Table V

Apparent Equilibrium Pressures at Different Temperatures

Temperature °C.	Pressure cm.Hg	Time hrs.	H_2 Pumped Off cc.
764°	1.35	10	0.7
764°	1.95	17	1.1
764°	2.00	21	---
799°	3.45	24	1.3
799°	3.42	24	---
835°	5.15	27	1.3
835°	5.45	47	---

On cooling the furnace to room temperature 14.1 cubic centimeters of the hydrogen produced by the final dissociation was not reabsorbed.

The iron reaction tube was removed and reweighed. The loss due to distillation after heating at 764°-835° C. for 170 hours was 0.0979 grams. A part of the calcium hydride was found to have sublimed in the form of pure white crystals on to the upper walls of the iron cylinder. The calcium hydride was ground in an agate mortar, quickly replaced in the iron cylinder and reweighed. The dissociation pressure was then redetermined at 835° C. and found to be 5.15 centimeters after 17 hours. The temperature was raised to 869° C., the pressure rising gradually to 7.1 centimeters and then falling slowly to 5.85 centimeters during the course of 20 hours. The dissociated hydrogen was not reabsorbed on cooling the furnace to room temperature. Pure white needle like sublimed crystals were again found in the upper portion of the iron cylinder.

The loss of weight due to distillation was 0.1260 grams. The results indicate that the dissociation pressures observed are not true equilibrium values. The amount of dissociation seems to increase with the time and the process is not reversible.

A 1.8103 gram sample of distilled calcium was next treated with hydrogen under high pressure at 250° C. 982.3 cubic centimeters of hydrogen were absorbed, 97 percent of the theoretical amount necessary to form the normal hydride.

Analysis.- Two samples of the 97 percent hydride were removed and analyzed for hydrogen by measuring the amount of hydrogen liberated when the sample was treated with water.

Anal. Subs., 0.2897, 0.2531. Calcd. for H, 4.76. Found 4.64, 4.59.

Dissociation pressure measurements were obtained with a 1.3431 gram sample of the 97 percent hydride. Adsorbed gases were pumped off up to 550°C., at which temperature dissociation first became apparent. Table VI gives the observed pressures obtained at 600°C., together with the amount of hydrogen pumped off and the time allowed for the pressure to become constant.

Table VI

Apparent Equilibrium Pressures at 600°C.

Pressure cm.Hg	Time hrs.	H_2 Pumped Off cc.
1.75	2.0	0.8
1.45	2.0	0.5
1.30	1.5	1.2
0.95	5.0	2.8

The furnace was cooled to room temperature, 2.8 cubic centimeters of hydrogen not being reabsorbed. The iron cylinder was removed and found to have lost 0.0030 grams. The cylinder was then immediately replaced, the system evacuated and adsorbed gases pumped off up to 500°. The first evidence of dissociation was again observed at approximately 550°. Another series of pressure measurements was obtained with the results shown in Table VII. No hydrogen was pumped off during this run.

Table VII

Dissociation Pressures at Different Temperatures

Temperature °C.	Pressure cm.Hg	Time hrs.
600°	0.55	2
700°	1.30	2
800°	2.60	1
800°	3.15	6

The furnace was cooled to 400°C and kept at this temperature overnight, the pressure falling to 2.4 centimeters during this time. Any free calcium in the system should have combined with the dissociated hydrogen at this temperature. The fact

that no hydrogen was absorbed is evidence that no free calcium was present. The furnace was again reheated, this time to 950° and another series of dissociation pressure measurements taken. The results are given in Table VIII.

Table VIII

Dissociation Pressures at Different Temperatures

Temperature °C.	Pressure cm.Hg	Time hrs.
950°	21.4	1.0
906°	13.3	0.75
852°	8.6	1.5
800°	4.8	1.5
754°	4.5	4.5
700°	4.35	43.0

The pressure was found to be sensitive to small changes in temperature in the region above 852°, but did not respond to such changes below this temperature. 11.95 cubic centimeters of hydrogen remained unabsorbed when the furnace was cooled to room temperature. The loss due to distillation was found to be 0.0143 grams.

The calcium hydride was powdered in an agate mortar, reweighed and quickly replaced in the apparatus. Adsorbed gases were pumped off up to 500°. The first evidence of dissociation was observed at 540°. The dissociation pressures were again redetermined. The values were first obtained at the lower temperatures with the results as shown in Table IX.

Table IX

Dissociation Pressures at Different Temperatures

Temperature °C	Pressure cm.Hg	Time hrs.
800°	2.6	2.0
852°	6.75	3.0
906°	11.10	0.75
950°	18.70	0.50

It will be observed that the pressures given in Table IX are lower than those shown in Table VIII, although only 11.95 cubic centimeters of hydrogen, which had not been reabsorbed, was removed.

The furnace was cooled to room temperature and the 10.73 cubic centimeters of hydrogen not reabsorbed pumped off. The quartz tube was then reheated to 852° and this temperature maintained for 179 consecutive hours. The changes in the dissociation pressure are shown in Table X.

Table X

Dissociation Pressures at 852° C.

Pressure cm.Hg	Time hrs.	H_2 Pumped Off cc.
4.8	2	5.6
3.5	2	4.2
3.9	24	----
5.6	55	----
6.5	79	----
7.5	105	----
8.8	155	----
9.4	179	----

The reaction tube was now cooled to room temperature, 23.6 cubic centimeters of hydrogen remaining unabsorbed. The

furnace was then reheated to 852°without removing the unabsorbed hydrogen and another series of dissociation pressures obtained. The results are given in Table XI.

Table XI

Dissociation Pressures at 852°C.

Pressure cm.Hg	Time hrs.
9.9	4
11.0	23
12.0	35
12.4	47
13.5	72
15.1	103

The furnace was cooled to room temperature, 36.9 cubic centimeters of hydrogen not being reabsorbed. This hydrogen was not reabsorbed after reheating the furnace for 11 hours at 500°C. The loss of weight due to distillation after heating at 852°C. for 282 hours was 0.2787 grams. A small amount of metallic calcium distilled above the furnace opening during the course of the experiment and considerable calcium hydride was found on the walls of the quartz tube at the level of the opening of the iron cylinder. This calcium hydride was probably formed by the action of some of the hydrogen with calcium which had first distilled on to the walls of the quartz tube.

A small amount of a hard gray-black solid was also found on the walls of the quartz tube. This material reacted very slowly with water, but dissolved readily in dilute

hydrochloric acid with the evolution of a spontaneously inflammable gas. The properties and chemical conduct of the gray-black solid indicate that it is calcium mono-silicide, Ca_2Si_2. Metallic calcium reacts with quartz at high temperatures to form calcium oxide and liberate silicon. The free silicon could then react with more calcium to form calcium monosilicide. Wöhler and Müller[1] state that calcium mono-silicide is acted on very slowly by cold water, but that dilute mineral acids decompose it vigorously with the evolution of silicon hydride. These facts are in agreement with the properties observed for the gray-black solid. The amount of material obtained was so small that it was impossible to scrape enough of it from the walls of the quartz tube for analysis.

No evidence of a true equilibrium was found in this experiment. The pressure continued to rise slowly during the entire 282 hours.

A 0.9396 gram sample of distilled calcium was next treated with hydrogen under high pressure at 250°. 524.8 cubic centimeters of hydrogen were absorbed, 99.9 percent of the theoretical amount necessary for the formation of normal calcium hydride. This almost pure hydride was then placed in a closed nickel cylinder, instead of in the open iron

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1. Wöhler and Müller, Z. anorg. Chem., 120, 49 (1921)

cylinder used in the previous experiments. The nickel cylinder, suggested by the work of Hurd and Walker,[1] was made from a rod of pure nickel 1.25 centimeters in diameter 9.0 centimeters in length and with a wall thickness of 0.75 millimeters. After placing the calcium hydride in the cylinder the open end was closed by driving in a tapered nickel plug. The nickel is permeable to hydrogen at high temperatures, but not to calcium and calcium hydride. The use of the closed tube thus prevents the loss of the solid products in the system by distillation.

Dissociation pressure measurements were obtained after pumping off adsorbed gases up to 500°. Table XII gives the dissociation pressures obtained at different temperatures, together with the total amounts of hydrogen removed and the time required for the pressure to reach the value given. In each case the pressure rose very slowly and reached a constant value only after prolonged heating. The pressures given, with the exception of the second, seventh and eighth, represent values which did not change when the furnace was heated for several additional hours.

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1. Hurd and Walker, loc. cit.

Table XII

Dissociation Pressures at Different Temperatures

Temperature °C.	Pressure cm.Hg	Time hrs.	H_2 Pumped Off cc.
852°	49.3	87	---
750°	28.6	10	---
700°	12.0	44	---
852°	49.3	17	---
852°	48.3	22	7.7
852°	47.3	43	21.5
852°	11.5	11	177.2
852°	11.3	24	202.6

It will be observed that the dissociation pressures given above are much higher than those obtained by any previous investigator and furnish additional evidence that the dissociation pressure is dependent on the composition of the solid phase.

The quartz tube was cooled rapidly to room temperature and the apparatus tested for leaks. The nickel cylinder was removed and found to be cracked about $\frac{3}{4}$ inch from the bottom. The loss of weight of the cylinder was 0.0597 grams. This low loss of weight indicates that the break must have occurred at the last of the experiment. The nickel was quite brittle at the point of the break, probably due to the formation of an alloy of nickel and calcium.

A fused metallic mass was found in the bottom of the cylinder, with a gray semi-crystalline material just above. A small amount of black solid had sublimed on to the bottom of the nickel plug.

Attempts to Prepare a Sub-Hydride of Calcium.-(a) By Addition of Approximately One Half the Theoretical Amount of Hydrogen Necessary to Form the Normal Hydride, at a Pressure Less Than the Apparent Equilibrium Pressure of the Normal Hydride.- Several attempts were made to prepare a calcium subhydride by adding hydrogen to calcium very slowly at temperatures from 754-792° and at pressures much lower than the apparent equilibrium values at these temperatures. Normal calcium hydride could not be formed under these conditions if the observed dissociation pressures are those of a true equilibrium. Table XIII gives the amount of hydrogen added, as well as the pressures and temperatures at which the gas was admitted.

Table XIII

Amounts of Hydrogen Added at Low Pressures

Weight of Ca used	H_2 Theoretical for CaH_2 cc.	H_2 Added cc.	Pressure cm. Hg	Temp. °C.
(1) 1.1193g.	628.0	284.0	0.1-1.0	792°
(2) 0.8083g.	451.9	227.3	0.1-1.0	785°
(3) 0.9547g.	533.7	317.7	0.1-1.0	785°
(4) 1.0469g.	585.3	100.0	0.1-0.5	782°
(5) 1.2815g.	716.3	223.0	0.1-0.8	785°
(6) 0.9785g.	547.0	253.0	0.1-1.0	790°
(7) 1.7513g.	979.0	894.0	0.1	754°
(8) 1.2706g.	710.0	351.7	0.1-0.4	788°

A dark gray powder was found in the iron cylinder in each case except number 7. Metallic calcium was found in the cylinder in those cases where the temperature had not been

raised above 790° after addition of the hydrogen. Considerable calcium always distilled on the cool portion of the quartz cylinder. This calcium remained as a dark shiny mirror.

Analysis.- The gray powder obtained in experiments 1 and 2 was analyzed for hydrogen by collection over acidulated water.

Anal. Subs., 0.1746, 0.0776, 0.0712. Calcd. for H (cc.) 141.2, 63.5, 58.9. Found 143.1, 63.6, 58.4.

The amount of hydrogen calculated was determined by assuming the gray powder to be calcium sub-hydride, Ca_2H_2, and postulating the following equation for the reaction: $Ca_2H_2 + 4HCl \rightleftharpoons 2CaCl_2 + 3H_2$. It should be noted that the same amount of hydrogen would also be liberated from a solid solution containing one mole of calcium for each mole of the normal hydride.

A small amount of black solid, probably calcium mono-silicide, which reacted very slowly with water, but dissolved readily in dilute hydrochloric acid with the evolution of a spontaneously inflammable gas, was always found on the walls of the quartz tube in the region of the opening of the iron cylinder. Small amounts of pure white needle like crystals of normal calcium hydride were found sublimed in the upper part of the iron cylinder in experiments 1, 3, 5 and 6.

Sample 4 was heated slowly after the addition of

100 cubic centimeters of hydrogen. The pressure was found to decrease as the temperature was raised, until no pressure showed on the manometer at 890°. Considerable calcium distilled on to the cool portion of the quartz tube during the heating and some black solid on to the hot portion. 0.07. grams of a black solid remained in the iron cylinder.

Samples 5 and 6 were heated to 916° after the addition of hydrogen. The pressure rose gradually to 7.1 centimeters in the case of sample 5 and to 8.05 centimeters in the case of sample 6.

Sample 7 was heated to 852° after addition of hydrogen. The dissociation pressure rose gradually to 2.6 centimeters and then decreased, the manometer showing no pressure after heating at 852° for one hour. The temperature was then raised to 900°, the pressure rising slowly to 4.25 centimeters during the course of 8 hours. The dissociated hydrogen was not reabsorbed when the reaction tube was cooled to room temperature. 0.3406 grams of a white semi-fused material remained in the iron cylinder. A large amount of the same material had distilled on to the walls of the quartz tube at the level of the opening of the iron cylinder.

Sample 8 was also heated to 852° after the addition of hydrogen at 788°. The pressure rose slowly to 0.45 centimeters and then decreased slowly, the manometer showing no pressure

after heating at 852° for 2½ hours. Rapid distillation of calcium occurred after the final pressure decrease. The temperature was maintained at 852° for an additional 12 hours. No dissociation pressure developed during this time, but more calcium distilled out. 0.1624 grams of a gray solid remained in the iron cylinder. Considerable light gray solid distilled on to the walls of the quartz tube just above the opening of the iron cylinder.

No conclusive evidence of the formation of a sub-hydride of calcium was found. The results seem to indicate that the gray solid obtained consists of a solid solution of calcium and calcium hydride as first postulated by Ephriam and Michel.

(b) Attempts to Obtain a Sub-Hydride of Calcium by Removal of Hydrogen from Normal Calcium Hydride.- Several samples of calcium hydride, prepared as described previously, were heated to a definite temperature and the dissociated hydrogen removed in small portions by allowing a definite volume of gas to expand into an evacuated reservoir. Table XIV gives the weight of calcium used, the amount of hydrogen added to form the normal hydride and the volume of hydrogen removed.

Table XIV

Amounts of Hydrogen Removed

Weight of Ca used	H_2 Added cc.	H_2 Removed cc.	Temperature °C.
(1) 0.6379g.	305.0	84.1	790°-1000°
(2) 0.7662g.	381.3	277.0	800°
(3) 1.3924g.	652.0	558.0	844°-960°
(4) 1.1029g.	481.6	242.6	726°-774°
(5) 0.6573g.	303.5	259.3	846°-862°
(6) 1.1500g.	567.5	442.0	726°-754°
(7) 4.6192g.	2370.0	468.8	960°
(8) 1.2833g.	604.3	111.6	800°-925°

A small amount of black solid, probably calcium mono-silicide, was found on the walls of the quartz tube in each experiment. The removal of hydrogen from the system always caused a slow decrease in pressure. In no case did the dissociation pressure return to its previous value, even after standing at constant temperature for many hours. A rapid distillation of calcium occurred after approximately one-half of the hydrogen first added was removed. A small amount of white material was usually found in the upper portion of the iron cylinder. A gray solid containing metallic particles was left in the bottom of the iron cylinder.

No evidence of the formation of a sub-hydride was found. The results again indicate that the dissociation pressure is dependent on the composition of the solid phase and that a solid solution of calcium and calcium hydride is probably formed when free calcium is present in the system.

DISCUSSION

As stated previously the results of the various investigators who have determined the dissociation pressures of calcium hydride differ widely. A comparison of the results of several workers is given in figure 4. The values given by Kassner and Stempel for what they claim to be the equilibrium $CaH_2 \rightleftharpoons CaH + \frac{1}{2}H_2$ are represented by circles, while the results of Moldenhauer and Roll-Hansen for what they believe to be the same equilibrium are represented by squares. The results of Hurd and Walker are represented by double circles and those of Kraus and Hurd by crosses. Moldenhauer and Roll-Hansen's determinations of what they call the sub-hydride equilibrium are represented by triangles.

It will be observed that the results of Moldenhauer and Roll-Hansen do not approach a straight line, while the determinations of Kraus and Hurd and Hurd and Walker are quite consistent and have nearly the same slope throughout. The results of Kassner and Stempel are subject to wider variation, but are fairly consistent.

Hurd and Walker and Remy-Cennette state that the pressure is independent of the amount of calcium present. These investigators find that the dissociation pressure remains constant when the proportion of hydride and calcium is varied between wide limits. The results obtained in this

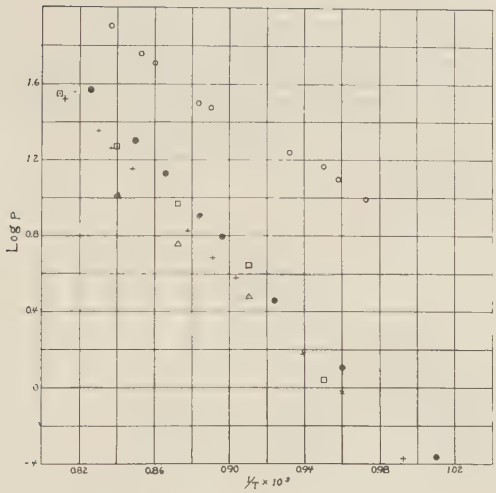

Fig. 4.- Comparison of Results of Several Investigators

investigation indicate that this is not the case.

The experimental data show that it has been possible to practically duplicate the results of all of the other workers in the field. Samples of calcium hydride of high hydrogen content have been found to give very high dissociation pressures, while mixtures of calcium and calcium hydride give much lower values. As has been pointed out before the results of this investigation seem to indicate the formation of a solid solution when free calcium is present in the system.

SUMMARY

1. Improved methods for the purification of calcium and of hydrogen have been described.

2. The adsorption of hydrogen by finely divided calcium at room temperature has been studied.

3. It has been shown that calcium and hydrogen react rapidly and quantitatively in the region of 250°C. to form calcium hydride, CaH_2.

4. Dissociation pressures of samples of calcium hydride of varying hydrogen content have been measured. No evidence of a true equilibrium has been found.

5. Attempts have been made to prepare a sub-hydride of calcium. No evidence for the existence of such a compound

has been found.

6. Calcium hydride and calcium appear to form a series of solid solutions with the dissociation pressure dependent on the composition of the solid phase.

In conclusion the author wishes to express his sincere thanks and appreciation to Dr. Warren C. Johnson, who suggested the problem and gave helpful guidance throughout the course of the investigation.